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(54) ADHESIVE SOFT ACRYLIC RESIN

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a soft acrylic resin composition; and an adhesive agent which comprises the soft acrylic resin composition and has an excellent performance.

SOLUTION: The acrylic resin composition comprises an acrylate monomer, a drying oil, an organic peroxide, an accelerator for decomposing an organic peroxide and a filler, wherein the acrylate monomer has at least one phenyl group in the molecule and can be polymerized to provide a product having an elongation of 200% or more at 20°C and a glass transition point of 0°C or less. The adhesive agent comprises the acrylic resin composition sandwiched between at least two release films.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the binder which consists of a flexible acrylic resin constituent. In more detail, adhesion increases with time amount after adhesion, and it is related with the binder which has the outstanding property which demonstrates firm adhesive strength.

[0002]

[Description of the Prior Art] Conventionally, that endurance is good and since it is environment-friendly, acrylic resin is broadly used in fields, such as a molding material, and a coating, adhesives. By adding organic peroxide as a polymerization initiator to an acrylic monomer or oligomer, and decomposing this organic peroxide thermally, such acrylic resin generates a radical, carries out the polymerization of an acrylic monomer or the oligomer, and is obtained.

[0003] After dissolving the above mentioned acrylic resin in a solvent conventionally, the binder which consists of acrylic resin blends an ingredient required for adhesion, removes the solvent to contain with heating etc. after applying on a release paper, and it twists and it is manufactured so that it may be put between a mold release film plane.

[0004] By such conventional approach, the equipment which manufactures acrylic resin, the equipment which blends an ingredient required for a binder, the equipment which dries spreading and a solvent to a mold releasing film are needed, and a large amount of investment is required for the manufacturing facility of a binder.

[0005] Furthermore, these solvents have many problems on air pollution or labor hygiene, and it looks forward to development of a binder with the sufficient engine performance which consists of acrylic resin of a non-solvent.

[0006]

[Problem(s) to be Solved by the Invention] This invention is to offer the binder which consists of acrylic resin of the non-solvent mold which does not need the large-scale above plant-and-equipment investment and which has the outstanding engine performance.

[0007]

[Means for Solving the Problem] This invention The acrylic ester monomer 100 mass section, drying oil 0.1 - 30 mass sections, And the decomposition accelerator of organic peroxide and organic peroxide and a filler are contained. It is the acrylic resin constituent whose young modulus of 20 degrees C is 5 or less MPas. Acrylic ester monomer 10 mass % [whose elongation of a polymerization object it has one phenyl group in 1 molecule at least, and is 200% or more at 20 degrees C] - 80 mass %, It is an acrylic resin constituent containing the acrylic ester monomer which the glass transition temperature of a polymerization object becomes more than from 0 degree C or less acrylic ester monomer 20 mass %, and is the binder which consists of an acrylic resin constituent which is inserted into the mold releasing film of at least two or more sheets, and exists.

[0008]

[Embodiment of the Invention] This invention only blends with an acrylic ester monomer the

decomposition accelerator which promotes disassembly of drying oil, and an organic peroxide and this peroxide, and does not need a special binder facility of the polymerization equipment needed when manufacturing acrylic resin conventionally, the dissolution facility to a solvent, etc., but an acrylic ester monomer can be easily resinified in ordinary temperature as flexible resin which has adhesiveness.

[0009] In the acrylic resin constituent of this invention, drying oil is incorporated in a lifting and a polymer in chain transfer at the place of the radical polymerization of an acrylic ester monomer, and forms bridge formation. However, the point that drying oil does not show the rise of the intense elastic modulus of an acrylic resin constituent resulting from the bridge formation formed at the place of the radical polymerization of an acrylic ester monomer when polyfunctional monomer is added is important.

[0010] Therefore, drying oil is a component required in order to use the acrylic resin constituent of this invention as soft resin.

[0011] Furthermore, drying oil has the property for which air was intercepted and which is hardened according to an operation of existence of oxygen, the decomposition accelerator of organic peroxide, etc., although it sees and it is thought by the upper sealing system that it is acting as a tackifier. Then, although the acrylic resin constituent of this invention made to put and exist in a release paper can strip a release paper and can be made to adhere to adherend, when a release paper is stripped, hardening of the part to which the front face of resin contacted air and contacted air is promoted. It is one of the important descriptions of this invention by making this hard facing cause moderately that the adhesion behavior which was markedly alike and was excellent as compared with the conventional binder, firmer adhesion, and adhesive strength can be obtained.

[0012] Although the acrylic resin constituent of this invention which followed, for example, puts and carried out the polymerization to the release paper can be made to adhere to adherend by removing a release paper, since it is exposed to air in the process in which a release paper is removed, after making adherend carry out adhesion, hardening advances further and pastes up more firmly the interface of the binder which consists of an acrylic resin constituent of adherend and this invention as compared with the conventional binder.

[0013] As an acrylic ester monomer which the acrylic resin constituent of this invention contains There are methacrylic ester and an acrylic ester (it is described as bitter taste rate below (meta)) system monomer. Specifically Methyl (meta) acrylate, ethyl (meta) acrylate, propyl (meta) acrylate, Butyl (meta) acrylate, 2-ethylhexyl (meta) acrylate, Iso octyl (meta) acrylate, iso octyl (meta) acrylate, Isodecyl (meta) acrylate, lauryl (meta) acrylate, A stearyl (meta) bitter taste rear chestnut rate, phenyl (meta) acrylate, Cyclohexyl (meta) acrylate, JISHIKURO pentenyl (meta) acrylate, JISHIKURO pentenyl (meta) acrylate, isobornyl (meta) acrylate, Methoxy-ized cyclo trien (meta) acrylate, JISHIKURO pentenyl oxy-ethyl (meta) acrylate, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, 3-hydroxypropyl (meta) acrylate, 4-hydroxy butyl (meta) acrylate, Polyethylene-glycol (meta) acrylate, alkyloxy polypropylene-glycol (meta) acrylate, Tetrahydrofurfuryl (meta) acrylate, 2-hydroxy-3-phenoxy propyl (meta) acrylate, Glycidyl (meta) acrylate, caprolactone conversion tetra-furfuryl (meta) acrylate, Ethoxy carbonylmethyl (meta) acrylate, phenol ethylene oxide conversion acrylate, PARAKU mill phenol ethylene oxide conversion acrylate, nonyl phenol ethylene oxide conversion acrylate, Nonyl phenol polypropylene oxide conversion acrylate, 2-ethylhexyl carbitol acrylate, Poly GURISERORUJI (meta) acrylate, Pori butylene glycol di(metha)acrylate, 1,4-butanediol (meta) acrylate, 1,6-hexanediol di(metha)acrylate, Neopentyl glycol di(metha)acrylate, TORIMECHI roll pro pantry (meta) acrylate, Epoxy (meta) acrylate, polyester (meta) acrylate, Urethane acrylate, acrylonitrile swine JIEN methacrylate, 2-hydroxy-3-phenoxypropylacrylate, phenol ethyleneoxide denaturation acrylate, PARAKU mill phenol ethyleneoxide denaturation acrylate, nonyl phenol ethyleneoxide denaturation acrylate, Phenol (two mol denaturation of ethyleneoxides) acrylate, phenol (four mol denaturation of ethyleneoxides) acrylate, Nonyl phenol (four mol denaturation of ethyleneoxides) acrylate, nonyl phenol (2 or 5 mol denaturation of ethyleneoxides) acrylate, etc. are mentioned.

[0014] Among these, the elongation of a polymerization object is 200% or more at 20 degrees C, and the

acrylic ester monomer which has one or more phenyl groups in a molecule at least is an especially desirable acrylic ester monomer.

[0015] Specifically, they are 2-hydroxy-3-phenoxypropylacrylate, phenol ethyleneoxide denaturation acrylate, PARAKU mill phenol ethyleneoxide denaturation acrylate, nonyl phenol ethyleneoxide denaturation acrylate, etc.

[0016] Furthermore, the glass transition temperature of a polymerization object is 0 degree C or less, and especially other desirable acrylic ester monomers that the acrylic resin system constituent of this invention contains are acrylic ester monomers which have one or more phenyl groups in a molecule at least.

[0017] Specifically, they are phenol (two mol denaturation of ethyleneoxides) acrylate, phenol (four mol denaturation of ethyleneoxides) acrylate, nonyl phenol (four mol denaturation of ethyleneoxides) acrylate, 2-ethylhexyl carbitol acrylate, 2.5 mol (propylene oxide) denaturation acrylate of nonyl phenol, etc.

[0018] These acrylic ester monomers may be used independently, and two or more kinds may use them, mixing in order to adjust the property of a constituent and a hardened material.

[0019] The acrylic ester monomer to which the elongation of a polymerization object of this invention has one or more phenyl groups in a molecule at least at 200% or more by 20 degrees C is a component to which carry out a hardened material flexibly and to which an elongation property is made to give, and it is desirable to contain more than 10 mass % in acrylic ester monomer 100 mass %.

[0020] The acrylic ester monomer to which the glass transition temperature of a polymerization object of this invention has one or more phenyl groups in a molecule at least below 0 degree C is a component which maintains the flexibility of a hardened material also in low temperature, and it is desirable to contain more than 20 mass % in acrylic ester monomer 100 mass %.

[0021] The drying oil used for this invention is the so-called glycerol ester of unsaturated fatty acid, such as linseed oil and boiled oil.

[0022] Drying oil is hardened in response to the effect of the oxygen in a polymerization initiator and air, in case an acrylic ester monomer carries out radical polymerization hardening.

[0023] Although many contents of drying oil are so desirable that there are, when many [too], chain transfer happens at the time of a radical polymerization, the molecular weight of the acrylic resin obtained falls, and there is a possibility of causing a strong fall. Therefore, especially the desirable loadings of desirable loadings are 3 - 20 mass section below 30 mass sections to the acrylic ester monomer 100 mass section.

[0024] The organic peroxide used for this invention for example, by hydroperoxide Tertiarybutyl hydroperoxide, A cumene hydroperoxide, JIISO pill benzene hydroperoxide, Paramenthane hydroperoxide, 2,5-dimethylhexane-2,5-dihydroperoxide, There is 1, 1, 3, and 3-tetramethyl BUCHIRUHAIDORO peroxide etc. In ketone peroxides, methyl ethyl ketone peroxide, cyclohexanon peroxide, Methylcyclohexanone peroxide, 3,3,5-trimethylcyclohexanone peroxide, There are methyl acetoacetate peroxide, acetylacetone peroxide, etc. To diacyl peroxide, acetyl peroxide, isobutyl peroxide, Octanol peroxide, decanol peroxide, RAURI Norian peroxide, benzoyl peroxide, 3 and 3, 5-trimethylhexanoyl peroxide, 2,4-dichlorobenzyl peroxide, etc. are mentioned.

[0025] The filler used for this invention can choose an ingredient suitably according to the application of an acrylic resin constituent. For example, in using it as a binder to prevent vibration, it uses a cheap rubber crumb, calcium-carbonate powder, etc.

[0026] Moreover, when using the acrylic resin constituent of this invention for the application which needs thermal conductivity, it is desirable to use metallic-oxide powder, such as silica powder, alumina powder, magnesia powder, boron nitride, aluminimium nitride, and ARUMINIMU powder.

[0027] Furthermore, in order to give fire retardancy to the acrylic resin constituent of this invention, it is desirable to add aluminum-hydroxide powder and silicic acid zinc powder.

[0028] As for these bulking agents, it is desirable to compound and use some kinds according to the purpose. Furthermore, a coloring agent, for example, a pigment, and a color may be added if needed.

[0029] When using the thing of a hydroperoxide mold or a ketone peroxide mold as organic peroxide,

metallic soap, an organic metal chelate, for example, octenate cobalt, naphthenic-acid cobalt, octenate nickel, naphthenic-acid nickel, octenate manganese, manganese naphthenate, and vanadium acetylacetonato can be used for the decomposition accelerator of the organic peroxide used for this invention.

[0030] Moreover, as a decomposition accelerator of other organic peroxide, the ethylenetiourea which are thiourea derivatives, benzyl thiourea, a diethylthio urea, dibutylthiourea, a tetra-methylthio urea, and its derivative can be used.

[0031] Furthermore, when using the organic peroxide of a diacyl peroxide mold like a benzoyl peroxide, an amines, for example, N, and N-dimethyl-P-toluidine, N, and N-diethyl-P-toluidine, N, and N-JI (2-hydroxyethyl)-P-toluidine, N, and N-JIPUROPA Norian-P-toluidine, N.N-dimethylaniline, ethyl diethanolamine, triethanolamine, etc. can be used as a decomposition accelerator of organic peroxide.

[0032] The acrylic resin constituent of this invention is the purpose which improves a property, and may blend a silane coupling agent, an elastomer, for example, acrylic rubber, polyurethane rubber, acrylonitrile-butadiene-styrene rubber, etc.

[0033]

[Example] Example 12-hydroxy-3-phenoxypropylacrylate (Toagosei ARONIKKUSU M-5700, 250% of elongation of hardened material) 60g, Nonyl phenol ethyleneoxide denaturation acrylate (Toagosei ARONIKKUSU M-111, 250% of elongation of hardened material) 10g, Four mol denaturation acrylate (Toagosei ARONIKKUSU M-113, glass transition temperature of -20 degrees C of hardened material) 30g of nonyl phenol ethyleneoxides, 0.3g (Nippon Unicar make A-174) of 6g (Kanto chemistry company reagent) silane coupling agents of linseed oil, Cumene hydroperoxide (Park Mill H80 by Nippon Oil & Fats Co., Ltd.) 3g and 250g (NSby Oriental milling company400N) of calcium-carbonate powder were thrown in, stirring mixing was carried out, and white ***** was obtained.

[0034] Subsequently, as an organic peroxide decomposition accelerator, addition mixing of the octenate cobalt (oct life Co12 by SHINTO fine chemical company) 1.5g was carried out, and it applied and rolled round to the release paper at about 1mm thickness. It resinified after 23 degrees C and 30 minutes. Furthermore, after leaving it for one week, when a release paper is removed, it is adhesive, and iron ***** which is plane-of-composition product 40mmx40mm carried out, and adhesion of the 23 degrees C of the two fixtures was carried out. It tore off, and using the hauling testing machine, it is a 20-degree C ambient atmosphere, and strong measurement was torn off and carried out by part for 10mm/in rate. It tore off and strong measurement was performed immediately after adhesion and after 23 degrees C and one-week care of health.

[0035]

粘着接着直後の引き剥がし強度	0. 2 0 M P a
2 3℃、1 週間養生後の引き剥がし強度	0. 4 2 M P a

[0036] The young moduli measured by part for 10mm/in 20 degrees C of the resin section which recuperated itself for one week at the aforementioned 23 degrees C, and hauling rate were 0.5MPa(s).

[0037] Example 22-hydroxy-3-phenoxypropylacrylate (Toagosei ARONIKKUSU M-5700, 250% of elongation of hardened material) 60g, Nonyl phenol ethyleneoxide denaturation acrylate (Toagosei ARONIKKUSU M-111, 250% of elongation of hardened material) 10g, Four mol denaturation acrylate (Toagosei ARONIKKUSU M-113, glass-transition-temperature--20 degree C of hardened material) 30g of nonyl phenol ethyleneoxides, 6g (Kanto chemistry company reagent) of linseed oil, 0.3g (Nippon Unicar make A-174) of silane coupling agents, N and N-JI (2-hydroxyethyl)-P-toluidine (Kanto chemistry company reagent) 1g, 0.1g (naphthenic-acid Mn6 by the SHINTO fine chemical company) of manganese naphthenate and 400g (AL[by Showa Denko K.K.]- 170) of alumina powder were thrown in, stirring mixing was carried out, and white ***** was obtained.

[0038] Subsequently, as organic peroxide, addition mixing of the 1.5g (NAIPAF by Nippon Oil & Fats

Co., Ltd.) of the benzoyl peroxides was carried out, and it applied and rolled round to the release paper at about 1mm thickness. After 23 degrees C and 30 minutes, the polymerization progressed and it resinified. Furthermore, after leaving it for one week, when the release paper was removed, resin had 23 degrees C of adhesiveness. With this adhesive resin, plane-of-composition product 40mmx40mm iron ***** carried out, and adhesion of the two fixtures was carried out. It tore off, and using the hauling testing machine, it is a 20-degree C ambient atmosphere, and strong measurement was torn off and carried out by part for 10mm/in rate. It tore off and strong measurement was performed immediately after adhesion and after 23 degrees C and one-week care of health.

[0039]

粘着接着直後の引き剥がし強度	0. 1 5 MP a
2 3℃、1 週間養生後の引き剥がし強度	0. 3 0 MP a

[0040] The young moduli measured by part for 10mm/in 20 degrees C of the resin which recuperated itself for one week at the aforementioned 23 degrees C, and hauling rate were 1.0MPa(s), and thermal conductivity was 1.8 W/m-k (JIS R-2618).

[0041] To up to the release paper, it applied to 2mm thickness and rolled round like the example 1, and 100 degrees C, the silicone resin system adhesives for example of comparison 1 vibrationproofing immobilization (Toshiba Silicone TSE3251) were heated for 5 hours, and were hardened. Subsequently, although the release paper was removed, there was no adhesiveness and it cannot be adhesion pasted up.

[0042] The room-temperature-curing mold silicone resin adhesives for example of comparison 2 heat dissipation (SE4420 by the Torre Silicone company) were applied to 2mm thickness on the release paper, it rolled round like the example 1, and 23 degrees C recuperated themselves for one week. Subsequently, although the release paper was removed, there was no adhesiveness and it cannot be adhesion pasted up.

[0043]

[Effect of the Invention] The technique in which a manufacturing facility is simple for the flexible acrylic resin of this invention, and it is very important for industrial manufacture of a vibroisolating material or a thermally conductive ingredient as a binder is offered.

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最終頁に続く

(54) 【発明の名称】 粘着性の柔軟なアクリル系樹脂

(57) 【要約】

【課題】 柔軟なアクリル系樹脂組成物、特に柔軟なアクリル系樹脂組成物からなる優れた性能を有する粘着剤を提供すること。

【解決手段】 アクリル酸エステルモノマー、乾性油、有機過酸化物、有機過酸化物の分解促進剤、充填材、を含有する柔軟なアクリル系樹脂組成物であり、少なくとも 1 分子中に 1 個のフェニル基を有し、かつ重合物の伸びが 20℃で 200%以上であるアクリル酸エステルモノマー、重合物のガラス転移温度が 0℃以下のアクリル酸エステルモノマーを含有する請求項 1 記載のアクリル系樹脂組成物であり、少なくとも 2 枚以上の離型フィルムに挟まれて存在するアクリル系樹脂組成物からなる粘着剤。

【特許請求の範囲】

【請求項1】 アクリル酸エステルモノマー100質量部、乾性油0.1～30質量部、および有機過酸化物、有機過酸化物の分解促進剤、充填材を含有し、20℃のヤングモジュラスが5MPa以下であるアクリル系樹脂組成物。

【請求項2】 少なくとも1分子中に1個のフェニル基を有し、かつ重合物の伸びが20℃で200%以上であるアクリル酸エステルモノマー10質量%～80質量%、重合物のガラス転移温度が0℃以下のアクリル酸エステルモノマー20質量%以上からなるアクリル酸エステルモノマーを含有する請求項1記載のアクリル系樹脂組成物。

【請求項3】 少なくとも2枚以上の離型フィルムに挟まれて存在する請求項1～2記載のアクリル系樹脂組成物からなる粘着剤

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、柔軟なアクリル系樹脂組成物からなる粘着剤に関する。さらに詳しくは粘着後に、時間とともに粘着力が増加し、強固な接着力を発揮する優れた性質を有する粘着剤に関する。

【0002】

【従来の技術】従来、アクリル系樹脂は、耐久性がよいこと、環境に優しいことなどから、成形材料や塗料、接着剤などの分野で幅広く利用されている。このようなアクリル系樹脂は、アクリル系モノマーやオリゴマーに重合開始剤として有機過酸化物を添加し、この有機過酸化物を加熱分解することにより、ラジカルを発生させアクリル系モノマーやオリゴマーを重合して得られる。

【0003】アクリル系樹脂からなる粘着剤は、従来、前記したアクリル系樹脂を溶剤に溶解してから、粘着に必要な材料を配合し、離型紙上に塗布後、含有する溶剤を加熱などで除去し、離型フィルム面に挟み込まれるように巻きつけて製造されている。

【0004】このような従来の方法では、アクリル系樹脂を製造する装置、粘着剤に必要な材料を配合する装置、離型フィルムに塗布、溶剤を乾燥する装置等が必要となり、粘着剤の製造設備に多額の投資が必要である。

【0005】更に、これらの溶剤は大気汚染や労働衛生上多くの問題を有しており、無溶剤のアクリル系樹脂からなる性能の良い粘着剤の開発が待望されている。

【0006】

【発明が解決しようとする課題】本発明は、上記のような大規模な設備投資を必要としない無溶剤型のアクリル系樹脂からなる、優れた性能を有する粘着剤を提供することにある。

【0007】

【課題を解決する手段】本発明は、アクリル酸エステルモノマー100質量部、乾性油0.1～30質量部、お

よび有機過酸化物、有機過酸化物の分解促進剤、充填材、を含有し、20℃のヤングモジュラスが5MPa以下であるアクリル系樹脂組成物であり、少なくとも1分子中に1個のフェニル基を有し、かつ重合物の伸びが20℃で200%以上であるアクリル酸エステルモノマー10質量%～80質量%、重合物のガラス転移温度が0℃以下のアクリル酸エステルモノマー20質量%以上からなるアクリル酸エステルモノマーを含有するアクリル系樹脂組成物であり、少なくとも2枚以上の離型フィルムに挟まれて存在するアクリル系樹脂組成物からなる粘着剤である。

【0008】

【発明の実施の形態】本発明は、アクリル酸エステルモノマーに、乾性油、および有機過酸化物と該過酸化物の分解を促進する分解促進剤等を単に配合するだけで、従来アクリル系樹脂を製造する際に必要とされていた重合装置や、溶剤への溶解設備などの特別な粘着剤設備を必要とせず、常温で容易にアクリル酸エステルモノマーを粘着性を有する柔軟な樹脂として樹脂化することができるものである。

【0009】本発明のアクリル系樹脂組成物において、乾性油は、アクリル酸エステルモノマーのラジカル重合の場で連鎖移動を起こし、重合体中に取り込まれ、架橋を形成する。しかしながら、アクリル酸エステルモノマーのラジカル重合の場で、多官能モノマーを添加した場合に形成される架橋に起因する、アクリル系樹脂組成物の激しい弾性率の上昇を、乾性油は示さない点が重要である。

【0010】したがって、乾性油は、本発明のアクリル系樹脂組成物を柔らかい樹脂にするために必要な成分である。

【0011】さらに、乾性油は、空気を遮断した見かけ上の密閉系では粘着付与剤として作用していると考えられるが、酸素の存在と、有機過酸化物の分解促進剤などの作用により硬化する性質がある。そこで、離型紙に挟み込んで存在させた本発明のアクリル系樹脂組成物は、離型紙をはがして被着体に粘着させることができるが、離型紙をはがしたときに、樹脂の表面が空気と接触し、空気と接触した部分の硬化が促進される。この表面硬化を、適度に起こさせることにより、従来の粘着剤と比較して格段に優れた、粘接着挙動、より強固な粘着力、接着力を得ることができることが本発明の重要な特徴の一つである。

【0012】したがって、例えば、離型紙に挟み込んで重合させた本発明のアクリル系樹脂組成物は、離型紙を除去することで被着体に粘着させることができるが、離型紙を除去する過程で空気に晒されるので、被着体に粘着接着させた後に、被着体と本発明のアクリル系樹脂組成物からなる粘着剤の界面は硬化が更に進行し、従来の粘着剤に比較して、より強固に接着するのである。

【0013】本発明のアクリル系樹脂組成物が含有する
 アクリル酸エステルモノマーとしては、メタクリル酸エ
 ステルとアクリル酸エステル（以下（メタ）アクリレート
 と記す）系モノマーがあり、具体的には、メチル（メ
 タ）アクリレート、エチル（メタ）アクリレート、プロ
 ピル（メタ）アクリレート、ブチル（メタ）アクリレ
 ート、2-エチルヘキシル（メタ）アクリレート、イソオ
 クチル（メタ）アクリレート、イソオクチル（メタ）ア
 クリレート、イソデシル（メタ）アクリレート、ラウリ
 ル（メタ）アクリレート、ステアシル（メタ）アクリ
 ア 10 クリレート、フェニル（メタ）アクリレート、シクロヘ
 キシル（メタ）アクリレート、ジシクロペンテニル（メ
 タ）アクリレート、ジシクロペンテニル（メタ）アクリ
 レート、イソボルニル（メタ）アクリレート、メトキシ
 化シクロトリエン（メタ）アクリレート、ジシクロペン
 テニルオキシエチル（メタ）アクリレート、2-ヒドロ
 キシエチル（メタ）アクリレート、2-ヒドロキシプロ
 ピル（メタ）アクリレート、3-ヒドロキシプロピル
 （メタ）アクリレート、4-ヒドロキシブチル（メタ）
 アクリレート、ポリエチレングリコール（メタ）アクリ
 20 レート、アルキルオキシポリプロピレングリコール（メ
 タ）アクリレート、テトラヒドロフルフリル（メタ）ア
 クリレート、2-ヒドロキシ-3-フェノキシプロピル
 （メタ）アクリレート、グリシジル（メタ）アクリレ
 ート、カプロラクトン変成テトラフルフリル（メタ）ア
 クリレート、エトキシカルボニルメチル（メタ）アクリ
 レート、フェノールエチレンオキシド変成アクリレート、
 パラクミルフェノールエチレンオキシド変成アクリレ
 ート、ノニルフェノールエチレンオキシド変成アクリレ
 30 レート、ノニルフェノールポリプロピレンオキシド変成ア
 クリレート、2-エチルヘキシルカルビトールアクリレ
 ート、ポリグリセロールジ（メタ）アクリレート、ポリブ
 チレングリコールジ（メタ）アクリレート、1,4-ブタ
 ジオール（メタ）アクリレート、1,6-ヘキサジオー
 ルジ（メタ）アクリレート、ネオペンチルグリコール
 ジ（メタ）アクリレート、トリメチロールプロパントリ
 （メタ）アクリレート、エポキシ（メタ）アクリレ
 ート、ポリエステル（メタ）アクリレート、ウレタンア
 クリレート、アクリロニトリルブタジエンメタクリレ
 ート、2-ヒドロキシ-3-フェノキシプロピルアクリレ
 40 レート、フェノールエチレンオキサライド変性アクリレ
 ート、パラクミルフェノールエチレンオキサライド変性ア
 クリレート、ノニルフェノールエチレンオキサライド変性ア
 クリレート、フェノール（エチレンオキサライド2モル変
 性）アクリレート、フェノール（エチレンオキサライド4
 モル変性）アクリレート、ノニルフェノール（エチレン
 オキサライド4モル変性）アクリレート、ノニルフェノ
 ール（エチレンオキサライド2,5モル変性）アクリレート
 等が挙げられる。

【0014】これらの内、重合物の伸びが20℃で20

0%以上で、少なくとも分子中に1個以上のフェニル基
 を有するアクリル酸エステルモノマーは特に好ましいア
 クリル酸エステルモノマーである。

【0015】具体的には、2-ヒドロキシ-3-フェノ
 キシプロピルアクリレート、フェノールエチレンオキサ
 イド変性アクリレート、パラクミルフェノールエチレン
 オキサライド変性アクリレート、ノニルフェノールエチレ
 ンオキサライド変性アクリレートなどである。

【0016】さらに、本発明のアクリル樹脂系組成物が
 含有する特に好ましい他のアクリル酸エステルモノマー
 は、重合物のガラス転移温度が0℃以下で、少なくとも
 分子中に1個以上のフェニル基を有するアクリル酸エス
 テルモノマーである。

【0017】具体的には、フェノール（エチレンオキサ
 イド2モル変性）アクリレート、フェノール（エチレン
 オキサライド4モル変性）アクリレート、ノニルフェノ
 ール（エチレンオキサライド4モル変性）アクリレート、2
 -エチルヘキシルカルビトールアクリレート、ノニルフ
 ェノール（プロピレンオキサライド）2,5モル変性アク
 リレートなどである。

【0018】これらのアクリル酸エステルモノマーは、
 単独で用いても良いし、組成物ならびに硬化物の性質を
 調整する目的で2種類以上混合して使用しても良い。

【0019】本発明の、重合物の伸びが20℃で200
 %以上で、少なくとも分子中に1個以上のフェニル基を
 有するアクリル酸エステルモノマーは、硬化物を柔軟に
 し、伸び特性を付与させる成分であり、アクリル酸エス
 テルモノマー100質量%中の10質量%以上含有する
 ことが好ましい。

30 【0020】本発明の、重合物のガラス転移温度が0℃
 以下で、少なくとも分子中に1個以上のフェニル基を有
 するアクリル酸エステルモノマーは、硬化物の柔軟性を
 低温に於いても維持させる成分であり、アクリル酸エス
 テルモノマー100質量%中の20質量%以上含有する
 ことが好ましい。

【0021】本発明に用いる乾性油は、例えば、亜麻仁
 油、ボイル油、など所謂、不飽和脂肪酸のグリセリンエ
 ステルである。

【0022】乾性油はアクリル酸エステルモノマーがラ
 ジカル重合硬化する際に、重合開始剤、および空気中の
 酸素の影響を受けて硬化する。

【0023】乾性油の含有量が多いほど好ましいが、多
 すぎるとラジカル重合時に連鎖移動が起こり、得られる
 アクリル系樹脂の分子量が低下し、強度の低下を引き起
 こす恐れがある。したがって好ましい配合量はアクリル
 酸エステルモノマー100質量部に対して、30質量部
 以下、特に好ましい配合量は3～20質量部である。

【0024】本発明に用いる有機過酸化物は、例えば、
 ハイドロパーオキサライド類ではターシャリブチルハイド
 50 ロパーオキサライド、クメンハイドロパーオキサライド、ジ

イソピルベンゼンハイドロパーオキシド、パラメンタンハイドロパーオキシド、2, 5-ジメチルヘキサン-2, 5-ジハイドロパーオキシド、1, 1, 3, 3-テトラメチルブチルハイドロパーオキシドなどがあり、ケトンパーオキシド類ではメチルエチルケトンパーオキシド、シクロヘキサノンパーオキシド、メチルシクロヘキサノンパーオキシド、3, 3, 5-トリメチルシクロヘキサノンパーオキシド、メチルアセトアセテートパーオキシド、アセチルアセトンパーオキシドなどがあり、ジアシルパーオキシド類にはアセチルパーオキシド、イソブチルパーオキシド、オクタノールパーオキシド、デカノールパーオキシド、ラウリノールパーオキシド、ベンゾイルパーオキシド、3, 3, 5-トリメチルヘキサノイルパーオキシド、2, 4-ジクロロベンゾイルパーオキシドなどが挙げられる。

【0025】本発明に用いる充填材は、アクリル系樹脂組成物の用途に応じて適宜材料を選択することができる。例えば、振動を防止する目的の粘着剤として使用する場合には、安価なゴム粉末、炭酸カルシウム粉末などを

【0026】また、本発明のアクリル系樹脂組成物を熱伝導性が必要な用途に使用する場合には、シリカ粉末、アルミナ粉末、マグネシア粉末、窒化ホウ素、窒化アルミニウム、アルミニウム粉などの金属酸化物粉末を使用することが好ましい。

【0027】更に、本発明のアクリル系樹脂組成物に難燃性を付与するためには、水酸化アルミニウム粉末や珪酸亜鉛粉末を添加することが好ましい。

【0028】これらの充填剤は目的に応じて、数種類を複合して用いることが好ましい。さらに、必要に応じて着色剤、例えば顔料や染料を添加しても良い。

【0029】本発明に用いる有機過酸化物の分解促進剤は、有機過酸化物としてハイドロパーオキシド型やケトンパーオキシド型のものを使用する場合には、金属石鹸や有機金属キレート、例えば、オクテン酸コバルト、ナフテン酸コバルト、オクテン酸ニッケル、ナフテン酸ニッケル、オクテン酸マンガ、ナフテン酸マンガ、バナジウムアセチルアセトナートを使用することができる。

【0030】また、他の有機過酸化物の分解促進剤としては、チオ尿素誘導体類であるエチレンチオ尿素、ベンジルチオ尿素、ジエチルチオ尿素、ジブチルチオ尿素、テトラメチルチオ尿素、およびその誘導体を使用するこ*

*とができる。

【0031】更に、過酸化ベンゾイルのようなジアシルパーオキシド型の有機過酸化物を使用する場合には、有機過酸化物の分解促進剤として、アミン類、例えば、N, N-ジメチル-P-トルイジン、N, N-ジエチル-P-トルイジン、N, N-ジ(2-ヒドロキシエチル)-P-トルイジン、N, N-ジプロパノール-P-トルイジン、N, N-ジメチルアニリン、エチルジエタノールアミン、およびトリエタノールアミンなどを使用することができる。

【0032】本発明のアクリル系樹脂組成物は、性質を改良する目的で、シランカップリング剤やエラストマー、例えば、アクリルゴム、ウレタンゴム、アクリロニトリル-ブタジエンスチレンゴム、などを配合してもよい。

【0033】

【実施例】実施例1

2-ヒドロキシ-3-フェノキシプロピルアクリレート（東亜合成社製アロニックスM-5700、硬化物の伸び250%）60g、ノニルフェノールエチレンオキシド変性アクリレート（東亜合成社製アロニックスM-111、硬化物の伸び250%）10g、ノニルフェノールエチレンオキシド4モル変性アクリレート（東亜合成社製アロニックスM-113、硬化物のガラス転移温度-20℃）30g、亜麻仁油（関東化学社試薬）6g

シランカップリング剤（日本ユニカ社製A-174）0.3g、クメンハイドロパーオキシド（日本油脂社製パークミルH80）3g、炭酸カルシウム粉（東洋製粉社製NS400N）250gを投入して攪拌混合して白色粘ちょう液を得た。

【0034】次いで、有機過酸化物分解促進剤として、オクテン酸コバルト（シントーファインケミカル社製オクトライフC012）1.5gを添加混合して、離型紙に約1mm厚さに塗布して巻き取った。23℃、30分後には樹脂化した。更に、23℃、1週間放置した後に、離型紙を剥がすと粘着性があり、接合面積40mm×40mmの鉄製引き剥がし治具2個を粘着接着した。引き剥がし強度の測定は引っ張り試験機を用い、20℃の雰囲気、引き剥がし速度10mm/分で実施した。引き剥がし強度の測定は粘着接着直後、および23℃、1週間養生後に行った。

【0035】

粘着接着直後の引き剥がし強度	0.20MPa
23℃、1週間養生後の引き剥がし強度	0.42MPa

【0036】前記の、23℃で1週間養生した樹脂部の20℃、引っ張り速度10mm/分で測定したヤングモジュラスは0.5MPaであった。

【0037】実施例2

2-ヒドロキシ-3-フェノキシプロピルアクリレート（東亜合成社製アロニックスM-5700、硬化物の伸び250%）60g、ノニルフェノールエチレンオキサイド変性アクリレート（東亜合成社製アロニックスM-111、硬化物の伸び250%）10g、ノニルフェノールエチレンオキサイド4モル変性アクリレート（東亜合成社製アロニックスM-113、硬化物のガラス転移温度-20℃）30g、亜麻仁油（関東化学社試薬）6g、シランカップリング剤（日本ユニカ社製A-174）0.3g、N,N-ジ（2-ヒドロキシエチル）-P-トリイジン（関東化学社試薬）1g、ナフテン酸マンガン（シントーファインケミカル社製 ナフテン酸Mn）※

*6) 0.1g、アルミナ粉末（昭和電工社製AL-170）400gを投入して攪拌混合して白色粘ちょう液を得た。

【0038】次いで、有機過酸化物として、過酸化ベンゾイル（日本油脂社製ナイパーF）1.5gを添加混合して、離型紙に約1mm厚さに塗布して巻き取った。23℃、30分後には重合が進み、樹脂化した。更に、23℃、1週間放置した後に、離型紙を剥がすと樹脂は粘着性があった。この粘着性樹脂により、接合面積40mm×40mmの鉄製引き剥がし治具2個を粘着接着した。引き剥がし強度の測定は引っ張り試験機を用い、20℃の雰囲気、引き剥がし速度10mm/分で実施した。引き剥がし強度の測定は粘着接着直後、および23℃、1週間養生後に行った。

【0039】

粘着接着直後の引き剥がし強度	0.15MPa
23℃、1週間養生後の引き剥がし強度	0.30MPa

【0040】前記の23℃で1週間養生した樹脂の、20℃、引っ張り速度10mm/分で測定したヤングモジュラスは1.0MPaであり、熱伝導率は1.8W/m・k（JIS R-2618）であった。

【0041】比較例1

防振固定用シリコン樹脂系接着剤（東芝シリコン（株）社製TSE3251）を離型紙上へ2mm厚さに塗布して、実施例1と同様に巻き取り、100℃、5時間加熱して硬化した。次いで、離型紙を除去したが、粘着性はなく、粘着接着不能であった。 ※

※【0042】比較例2

放熱用室温硬化型シリコン樹脂接着剤（トーレ・シリコン（株）社製 SE4420）を離型紙上へ2mm厚さに塗布して、実施例1と同様に巻き取り、23℃、1週間養生した。次いで、離型紙を除去したが、粘着性はなく、粘着接着不能であった。

【0043】

【発明の効果】本発明の柔軟なアクリル系樹脂は製造設備も簡単で、粘着剤として防振材や熱伝導性材料の工業的な製造に極めて重要な技術を提供するものである。

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(54) **CURABLE RESIN COMPOSITION**

(57) It is to provide a curable resin composition which is curable at room temperature, has fluidity, is excellent in workability and provides a cured product having high thermal conductivity and being excellent in flexibility.

A curable resin composition comprising a (meth)acrylate monomer, an organic peroxide, a decomposition accelerator for the organic peroxide, and an inorganic filler, wherein the inorganic filler has a particle size distribution such that it has peak diameters at least in the respective regions of from 3 to 10 μm and from 30 to 70 μm , and the mode diameter is from 30 to 70 μm and the median diameter is from 5 to 40 μm .

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Description

TECHNICAL FIELD

[0001] The present invention relates to a curable resin composition applicable to a potting material to seal electronic components and an adhesive to be used for bonding e.g. heat spreaders and heatsinks in semiconductor packages. Particularly, it relates to a curable resin composition which is excellent in fluidity even when it contains an inorganic filler and is curable at room temperature without heating, which provides a cured product being flexible and having high thermal conductivity, and is thereby applicable to potting materials and adhesives.

BACKGROUND ART

[0002] Potting treatment and the like by e.g. an epoxy resin or a silicone resin have been widely employed for the purpose of insulation, moisture-proofing, waterproofing, or vibration-proofing for electronic components. Further, along with e.g. downsizing, increase in density and increase in power of electronic components in recent years, as a potting material therefor, e.g. an epoxy resin and a silicone resin into which an inorganic filler having thermal conductivity such as silica or alumina is incorporated for the purpose of releasing heat generated from the electronic components, have been used. Further, for semiconductor packages also, a means for heat dissipation has been employed by bonding heat spreaders or heatsinks for the purpose of protecting e.g. IC chips from heat generation. Similarly, along with downsizing and increase in density of electronic components, bonding by an adhesive, not by screws, has been carried out, and as the adhesive, e.g. an epoxy resin and a silicone resin having thermal conductivity have been used.

[0003] An epoxy resin into which an inorganic filler is incorporated has excellent heat insulation properties and water resistance, but its cured product has a very high modulus, whereby a stress is likely to be applied to e.g. components by e.g. heat shock, which may cause cracks or separation. Further, in the case of a two part epoxy resin, there is a risk of insufficient curing if the blend ratio of the curing agent is mistaken. On the other hand, in the case of a one part epoxy resin, a heating apparatus is required in many cases and the curing time tends to be long, such being disadvantageous in view of further labor saving and energy saving and shortening of operation time.

[0004] Further, a silicone resin has been known as a RTV (room temperature vulcanizable) rubber, and its cured product has low hardness and is excellent in low temperature resistance and heat resistance. However, a silicone resin has such drawbacks that a low molecular siloxane contained as an impurity may cause continuity failure or abrasion of electric contacts, and is expensive also.

[0005] On the other hand, heretofore, an acrylic resin has been widely used in the field of molding materials, coatings and adhesives by virtue of having good durability and being environmentally friendly. Such an acrylic resin may be obtained in such a manner that an organic peroxide as a polymerization initiator is added to an acrylic monomer or oligomer, and radicals are generated by thermolysis of the organic peroxide to polymerize the acrylic monomer or oligomer.

[0006] An acrylic resin is characterized in that it is generally less extendable and its cured product is hard. Further, if an inorganic filler is incorporated, it will have a high modulus in the same manner as an epoxy resin and be poor in heat cycle resistance. However, in recent years, by e.g. use of an acrylic monomer to impart flexibility, an acrylic resin being flexible and having a low modulus equal to a silicone resin has been developed.

[0007] However, even with respect to such an acrylic resin having flexibility imparted, if an inorganic filler to impart thermal conductivity is incorporated in a large amount, the viscosity tends to increase, and when an electronic component is sealed or bonded, workability tends to be poor and it cannot sufficiently infiltrate into the component, or the sealed or bonded resin itself may contain bubbles, and no sufficient heat dissipation properties can be secured (Patent Documents 1 and 2).

Patent Document 1: JP-B-54-28178

Patent Document 2: JP-A-2002-308919

DISCLOSURE OF THE INVENTION

OBJECT TO BE ACCOMPLISHED BY THE INVENTION

[0008] As described above, development of a potting material and an adhesive which have higher fluidity and good workability as compared with conventional potting material and adhesive, have high thermal conductivity and moderate hardness, and provide a cured product excellent in heat cycle resistance, have been desired.

[0009] The present invention is to provide a curable resin composition having thermal conductivity with which heat

generated from electronic components can be released, which is curable at room temperature and which has fluidity, and a potting material and an adhesive excellent in workability which are made of the curable resin composition, thereby to dissolve the problems of the above prior art.

5 MEANS TO ACCOMPLISH THE OBJECT

[0010] The present invention provides a curable resin composition comprising a (meth)acrylate monomer, an organic peroxide, a decomposition accelerator for the organic peroxide, and an inorganic filler, wherein the inorganic filler has a particle size distribution such that it has peak diameters at least in the respective regions of from 3 to 10 μm and from 30 to 70 μm , and the mode diameter is from 30 to 70 μm and the median diameter is from 5 to 40 μm ; the curable resin composition wherein the inorganic filler has a particle size distribution such that it has peak diameters at least in the respective regions of from 0.2 to 1.5 μm , from 3 to 10 μm and from 30 to 70 μm , the mode diameter is from 30 to 70 μm and the medium diameter is from 5 to 40 μm ; the curable resin composition which comprises from 0.5 to 10 parts by mass of the organic peroxide, from 0.1 to 10 parts by mass of the decomposition accelerator and from 100 to 1,500 parts by mass of the inorganic filler, respectively, per 100 parts by mass of the (meth)acrylate monomer; the curable resin composition further containing a drying oil, which comprises from 1 to 30 parts by mass of the drying oil, from 0.5 to 10 parts by mass of the organic peroxide, from 0.1 to 10 parts by mass of the decomposition accelerator and from 100 to 1,500 parts by mass of the inorganic filler, respectively, per 100 parts by mass of the (meth)acrylate monomer; the curable resin composition, wherein the inorganic filler is spherical alumina; and a cured product, a potting material and an adhesive, each made of the above curable resin composition.

EFFECTS OF THE INVENTION

[0011] The curable resin composition of the present invention has fluidity and is excellent in workability and further, it is curable at room temperature and is thereby advantageous in labor saving, energy saving and shortening of operation time. Further, its cured product has thermal conductivity with which heat generated from electronic components can be sufficiently released, and is flexible and has low modulus, and has favorable heat cycle resistance, and is thereby excellent in environmental resistance.

30 BEST MODE FOR CARRYING OUT THE INVENTION

[0012] The (meth)acrylate monomer contained in the curable resin composition of the present invention is a methacrylate or acrylate (hereinafter referred to as (meth)acrylate) monomer, and specifically, it may, for example, be methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, isooctyl (meth)acrylate, isodecyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, phenyl (meth)acrylate, cyclohexyl (meth)acrylate, dicyclopentanyll (meth)acrylate, dicyclopentenyl (meth)acrylate, dicyclopentenylloxyethyl (meth)acrylate, isobornyl (meth)acrylate, methoxylated cyclodecatrien (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, alkyloxy polyethylene glycol mono(meth)acrylate, alkyloxy polypropylene glycol mono(meth)acrylate, tetrahydrofurfuryl(meth)acrylate, 2-hydroxy-3-phenoxypropyl (meth)acrylate, glycidyl (meth)acrylate, caprolactone modified tetrahydrofurfuryl(meth)acrylate, 3-chloro-2-hydroxypropyl (meth)acrylate, N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, t-butylaminoethyl (meth)acrylate, morpholine (meth)acrylate, ethoxycarbonylmethyl (meth)acrylate, phenol ethylene oxide modified acrylate, phenol (ethylene oxide 2 mol modified) acrylate, phenol (ethylene oxide 4 mol modified) acrylate, p-cumylphenol ethylene oxide modified acrylate, nonylphenol ethylene oxide modified acrylate, nonylphenol (ethylene oxide 4 mol modified) acrylate, nonylphenol (ethylene oxide 8 mol modified) acrylate, nonylphenol (propylene oxide 2.5 mol modified) acrylate, 2-ethylhexylcarbitol acrylate, polyglycerol di(meth)acrylate, polybutylene glycol di(meth)acrylate, 1,4-butanediol (meth)acrylate, 1,6-hexanediol (meth)acrylate, neopentyl glycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, (meth)acrylate of ethylene oxide modified phthalic acid, (meth)acrylate of ethylene oxide modified succinic acid, trifluoroethyl (meth)acrylate, tetrafluoropropyl (meth)acrylate, 1,2-polybutadiene terminal urethane modified di(meth)acrylate, polyacrylonitrile butadiene methacrylate, 2,2-bis(4-(meth)acryloxydiethoxyphenyl)propane, 2,2-bis(4-(meth)acryloxypropoxyphenyl)propane, 2,2-bis(4-(meth)acryloxytetraethoxyphenyl)propane, epoxy acrylate, urethane acrylate or polyester (meth)acrylate.

[0013] Among them, a (meth)acrylate monomer having at least one phenyl group in its molecule is particularly preferred as the (meth)acrylate monomer to be contained in the curable resin composition of the present invention, since a homopolymer of the (meth)acrylate monomer has an elongation of at least 200% at 20°C.

[0014] Specifically, the (meth)acrylate monomer may, for example, be preferably 2-hydroxy-3-phenoxypropyl acrylate, phenol ethylene oxide modified acrylate, p-cumylphenol ethylene oxide modified acrylate or nonylphenol ethylene oxide

modified acrylate.

[0015] Further, another particularly preferred (meth)acrylate monomer to be contained in the curable resin composition of the present invention is a (meth)acrylate monomer having at least one phenyl group in its molecule, which provides a homopolymer of the (meth)acrylate monomer having a glass transition temperature of at most 0°C.

[0016] Specifically, another (meth)acrylate monomer may, for example, be preferably phenol (ethylene oxide 2 mol modified) acrylate, phenol (ethylene oxide 4 mol modified) acrylate, nonylphenol (ethylene oxide 2 mol modified) acrylate, nonylphenol (ethylene oxide 4 mol modified) acrylate, nonylphenol (ethylene oxide 8 mol modified) acrylate, nonylphenol (propylene oxide 2.5 mol modified) acrylate, nonylphenoxypolyethylene glycol methacrylate, nonylphenoxypolypropylene glycol methacrylate, nonylphenoxypoly(ethylene glycol-polypropylene) methacrylate, phenoxyethyl acrylate or phenoxyethyl methacrylate.

[0017] These (meth)acrylate monomers may be used alone or as a mixture of at least two for the purpose of adjusting adhesive properties, curing properties and physical properties of a cured product.

[0018] In the curable resin composition of the present invention, the (meth)acrylate monomer having at least one phenyl group in its molecule, which provides a homopolymer of the (meth)acrylate monomer having an elongation of at least 200% at 20°C, is a component which makes a cured product be flexible and which imparts elongation properties. This (meth)acrylate monomer is contained preferably in an amount of at least 10 mass% in 100 mass% of all the (meth)acrylate monomers.

[0019] In the curable resin composition of the present invention, the (meth)acrylate monomer having at least one phenyl group in its molecule, which provides a homopolymer of the (meth)acrylate monomer having a glass transition temperature of at most 0°C, is a component which makes flexibility of a cured product be maintained even at low temperature. This (meth)acrylate monomer is contained preferably in an amount of at least 20 mass% in 100 mass% of all the (meth)acrylate monomers.

[0020] In the curable resin composition of the present invention, a drying oil will bring chain transfer at the site of radical polymerization of the (meth)acrylate monomer, be incorporated in the polymer and form crosslinks. Further, the drying oil has such a function that a peroxide is formed by the action of the air, which is decomposed by a decomposition accelerator for the organic peroxide to form free radicals, thereby to polymerize a monomer, i.e. so-called air-curing properties.

[0021] A compound having air-curing properties may, for example, be a dicyclopentenyl (meth)acrylate monomer, a dicyclopentenylxyethyl (meth)acrylate monomer, a dicyclopentadiene resin or a (meth)acrylate modified polybutadiene. However, each of them will drastically increase the modulus, and none of them can be added in an amount in which the air-curing properties can be obtained.

[0022] Accordingly, the drying oil is a component required to impart air-curing properties, in addition to making the curable resin composition of the present invention be a flexible resin.

[0023] The drying oil to be used in the present invention is a glycerol ester of an unsaturated fatty acid, such as linseed oil, boiled oil or fish oil.

[0024] The content of the drying oil is preferably higher in view of flexibility and air-curing properties, but if it is too high, chain transfer will occur at the time of radical polymerization, whereby the molecular weight of a (meth)acrylic resin to be obtained will decrease, which may cause a decrease in strength. Accordingly, a preferred blending amount is from 1 to 30 parts by mass, particularly preferably from 3 to 20 parts by mass, per 100 parts by mass of the (meth)acrylate monomer.

[0025] If the content of the drying oil is less than 1 part by mass, the surface drying effect will be insufficient, and the inorganic filler incorporated will not be maintained in the interior of a cured product and will come to the surface to be in contact with the air of the cured product, such being unfavorable.

[0026] The organic peroxide to be used as a polymerization initiator for the curable resin composition of the present invention may, for example, be a hydroperoxide such as tert-butyl hydroperoxide, cumene hydroperoxide, diisopropylbenzene hydroperoxide, p-menthane hydroperoxide, 2,5-dimethylhexane-2,5-dihydroperoxide or 1,1,3,3-tetramethylbutyl hydroperoxide, a ketone peroxide such as methyl ethyl ketone peroxide, cyclohexanone peroxide, 3,3,5-trimethylcyclohexanone peroxide, methylcyclohexanone peroxide, methylacetoacetate peroxide or acetylacetone peroxide, or a diacyl peroxide such as acetyl peroxide, isobutyl peroxide, octanoyl peroxide, decanoyl peroxide, lauronyl peroxide, 3,3,5-trimethylhexanoyl peroxide, succinic acid peroxide, benzoyl peroxide, 2,4-dichlorobenzoyl peroxide or m-toluoyl peroxide.

[0027] These organic peroxides may be used alone or in combination of two or more of them.

[0028] The amount of the organic peroxide used is preferably from 0.5 to 10 parts by mass per 100 parts by mass of the (meth)acrylate monomer. If it is less than 0.5 part by mass, curing will be insufficient, and if it exceeds 10 parts by mass, adhesive properties will rather decrease, storage stability will remarkably decrease and further, skin irritativeness will be intense, such being unfavorable.

[0029] The decomposition accelerator for the organic peroxide of the present invention may, in the case of using as the organic peroxide a hydroperoxide or a ketone peroxide, for example, be a metal salt of an organic acid or an organic

metal chelate, such as cobalt naphthenate, copper naphthenate, manganese naphthenate, cobalt octanoate, copper octanoate, manganese octanoate, copper acetylacetonate, titanium acetylacetonate, manganese acetylacetonate, chromium acetylacetonate, iron acetylacetonate, vanadium acetylacetonate or cobalt acetylacetonate.

[0030] Further, another decomposition accelerator for the organic peroxide may, for example, be a thiourea derivative such as diethylthiourea, dibutylthiourea, ethylenethiourea, tetramethylthiourea, mercaptobenzoimidazole or benzoylthiourea.

[0031] Further, in a case where a diacyl peroxide such as benzoyl peroxide is used as the organic peroxide, the decomposition accelerator for the organic peroxide may, for example, be an amine such as N,N-dimethyl-p-toluidine, N,N-diethyl-p-toluidine, N,N-di(2-hydroxyethyl)-p-toluidine, N,N-diisopropanol-p-toluidine, triethylamine, tripropylamine, ethyldiethanolamine, N,N-dimethylaniline, ethylenediamine, triethanolamine or an aldehyde-amine condensation product.

[0032] These decomposition accelerators for the organic peroxide may be used alone or in combination of two or more of them.

[0033] The amount of the decomposition accelerator for the organic peroxide in the present invention is preferably from 0.1 to 10 parts by mass per 100 parts by mass of the (meth)acrylate monomer. If it is less than 0.1 part by mass, curing tends to be insufficient, and if it exceeds 10 parts by mass, adhesive properties may decrease or storage stability may decrease.

[0034] Particles of the inorganic filler to be used for the curable resin composition of the present invention are required to have a particle size distribution such that it has peak diameters at least in the respective regions of from 3 to 10 μm and from 30 to 70 μm , and the mode diameter is from 30 to 70 μm and the medium diameter is from 5 to 40 μm . More preferably, they have a particle size distribution such that it has peak diameters at least in the respective regions of from 0.2 to 1.5 μm , from 3 to 10 μm and from 30 to 70 μm , and the mode diameter is from 30 to 70 μm and the medium diameter is from 5 to 40 μm .

[0035] Particles of the inorganic filler showing a peak diameter in a region of from 30 to 70 μm are particles to be nuclei when the inorganic filler is incorporated into the resin, and if the peak diameter is less than 30 μm , the viscosity of the curable resin composition will remarkably increase, and if it exceeds 70 μm , a coarse powder will undergo sedimentation apart from the (meth)acrylate monomer during storage or during potting of electronic components, or small spaces of the electronic components may be clogged with the coarse powder and it cannot penetrate to the electronic components. Further, particles showing a peak diameter in a region of from 3 to 10 μm can penetrate into spaces between particles showing a peak diameter in a region of from 30 to 70 μm and make a dense particle packing structure, whereby the viscosity can be decreased by the closest packing effect. By the particle size distribution having these two peak diameters simultaneously, a decrease in viscosity when the inorganic filler is incorporated at a high density, which has not been accomplished, can be achieved.

[0036] More preferably, the particle size distribution has, in addition to the above two peak diameters, a peak diameter in a region of from 0.2 to 1.5 μm . The particles showing a peak diameter in a region of from 0.2 to 1.5 μm can penetrate into spaces in the particle packing structure comprising particles showing a peak diameter in a region of from 30 to 70 μm and particles showing a peak diameter in a region of from 3 to 10 μm , and they can make a denser particle packing structure, whereby the viscosity of the curable resin composition can be more decreased.

[0037] The peak diameter in the present invention is a particle diameter showing a peak in the frequency particle size distribution of the inorganic filler. The mode diameter is the most frequent diameter among the peak diameters, and the medium diameter is a cumulative 50 wt% particle diameter in the cumulative particle size distribution. The particle size distribution can be measured by a laser diffraction light-scattering method.

[0038] The inorganic filler in the present invention may, for example, be an oxide such as spherical alumina, powdered alumina, magnesium oxide, beryllium oxide or titanium oxide; a nitride such as boron nitride, silicon nitride or aluminum nitride; a carbide such as silicon carbide; a hydrated metal such as aluminum hydroxide or magnesium hydroxide; a metal filler of e.g. copper, silver, iron, aluminum or nickel; a metal alloy filler of e.g. titanium, a carbon type filler of e.g. diamond or carbon; quartz, quartz glass, or a silica powder of e.g. fused silica or spherical silica. These inorganic fillers may be used alone or in combination of two or more of them. Among these inorganic fillers, particularly preferred is spherical alumina or spherical silica in view of availability and incorporation properties into the acrylic resin, and more preferably, spherical alumina is most suitable in view of thermal conductivity.

[0039] The amount of the inorganic filler of the present invention is preferably from 10 to 1,500 parts by mass per 100 parts by mass of the (meth)acrylate monomer. If it is less than 1 part by mass, no thermal conductivity will be imparted. If it exceeds 1,500 parts by mass, a mixture for the curable resin composition will be clayey and will have no fluidity, such being unfavorable from the viewpoint of workability and adhesive properties.

[0040] For the curable resin composition of the present invention, a small amount of a polymerization inhibitor may be used to improve the storage stability of the composition. The polymerization inhibitor may, for example, be methylhydroquinone, hydroquinone, 2,2-methylene-bis(4-methyl-6-tert-butylphenol), catechol, hydroquinone monomethyl ether, mono tert-butylhydroquinone, 2,5-di-tert-butylhydroquinone, p-benzoquinone, 2,5-diphenyl-p-benzoquinone, 2,5-

di-tert-butyl-p-benzoquinone, picric acid, citric acid, phenothiazine, tert-butylcatechol, 2-butyl-4-hydroxyanisole or 2,6-di-tert-butyl-p-cresol.

[0041] The amount of the polymerization inhibitor is preferably from 0.001 to 3 parts by mass, more preferably from 0.01 to 2 parts by mass per 100 parts by mass of the (meth)acrylate monomer. If it is less than 0.001 part by mass, the storage stability will decrease, and if it exceeds 3 parts by mass, adhesive properties are likely to decrease, whereby the curable resin composition may be uncured.

[0042] For the curable resin composition of the present invention, a coupling agent may be used in combination for the purpose of improving fluidity. The coupling agent may, for example, be a silane coupling agent or a titanate coupling agent.

[0043] The silane coupling agent may, for example, be γ -chloropropyltrimethoxysilane, vinyltrimethoxysilane, vinyltrichlorosilane, vinyltriethoxysilane, vinyl-tris(β -methoxyethoxy)silane, γ -methacryloxypropyltrimethoxysilane, γ -acryloxypropyltrimethoxysilane, β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, γ -glycidoxypropyltrimethoxysilane, γ -mercaptopropyltrimethoxysilane, γ -aminopropyltriethoxysilane, N- β -(aminoethyl)- γ -aminopropyltrimethoxysilane, N- β -(aminoethyl)- γ -aminopropylmethyldimethoxysilane or γ -ureidopropyltriethoxysilane.

[0044] The titanate coupling agent may, for example, be isopropyltriisostearoyl titanate, isopropyltridecylbenzenesulfonfyl titanate, isopropyltris(dioctylpyrophosphate) titanate, tetraisopropylbis(dioctylphosphite) titanate, tetraoctylbis(ditridecylphosphite) titanate, tetra(2,2-dialyloxy-1-butyl)bis(ditridecylphosphite) titanate, bis(dioctylpyrophosphate)oxyacetate titanate, bis(dioctylpyrophosphate)ethylene titanate, isopropyltriocanoyl titanate, isopropylidimethacrylisostearoyl titanate, isopropylisostearoyldiacryl titanate, isopropylisotri(dioctylphosphate) titanate, isopropyltricumylphenyl titanate, isopropyltri(N-aminoethyl-aminoethyl) titanate, dicumylphenyloxyacetate titanate or diisostearoylethylene titanate.

[0045] The amount of the silane coupling agent or the titanate coupling agent used is preferably from 0.001 to 10 parts by mass per 100 parts by mass of the (meth)acrylate monomer. If it is less than 0.001 part by mass, no effect will be obtained, and if it exceeds 10 parts by mass, adhesive properties may decrease.

[0046] For the curable resin composition of the present invention, it is possible to use additives which are commonly used, such as an elastomer such as an acrylic rubber, a urethane rubber or an acrylonitrile-butadienestyrene rubber, a solvent, a bulk filler, a reinforcing material, a plasticizer, a thickener, a chelating agent, a dye, a pigment, a fire retardant and a surfactant, within a range not to impair the object of the present invention.

[0047] The curable resin composition of the present invention is used usually by mixing the (meth)acrylate monomer, the drying oil, the organic peroxide, the decomposition accelerator for the organic peroxide and the inorganic filler with stirring. The curable resin composition of the present invention may be used as a one part or two part potting material or adhesive. For example, in the case of a one part type, preferred is a method of preliminarily mixing the (meth)acrylate monomer, the drying oil, the organic peroxide and the inorganic filler component, and adding the decomposition accelerator for the organic peroxide at the time of use. In the case of a two part type, for example, a method may be mentioned wherein a mixture of the (meth)acrylate monomer and the inorganic filler is divided to two parts, the organic peroxide is added to one part (component A) and the decomposition accelerator for the organic peroxide is added to the other part (component B), and the components A and B are mixed at the time of use. On that occasion, in order to secure the storage stability, the entire drying oil is preferably incorporated into the component A containing the organic peroxide.

EXAMPLES

[0048] Now, the present invention will be explained in further detail with reference to Examples. However, the present invention is by no means restricted to such specific Examples.

EXAMPLE 1, COMPARATIVE EXAMPLE 1

[0049] As an inorganic filler, 9 types of spherical alumina with different particle size distributions were prepared. The peak diameters of these spherical alumina powders in regions in the vicinity of from 0.2 to 1.5 μm , from 3 to 10 μm and from 30 to 70 μm are shown in Table 1.

TABLE 1

Spherical alumina No.	Peak diameter (μm) in 0.2 to 1.5 μm	Peak diameter (μm) in 3 to 10 μm	Peak diameter (μm) in 30 to 70 μm	Mode diameter (μm)	Median diameter (μm)
I	0.3	5.2	38.8	38.8	9.5
II	0.3	7.5	38.8	38.8	12.1
III	0.7	7.5	55.1	55.1	12.0

(continued)

Spherical alumina No.	Peak diameter (μm) in 0.2 to 1.5 μm	Peak diameter (μm) in 3 to 10 μm	Peak diameter (μm) in 30 to 70 μm	Mode diameter (μm)	Median diameter (μm)
IV	Nil	5.2	38.8	38.8	23.5
V	0.7	5.1	76.1	76.1	35.9
VI	0.3	15.5	38.8	38.8	17.6
VII	0.1	Nil	38.8	38.8	35.3
VIII	0.3	5.2	25.7	25.7	11.9
IX	0.7	3.2	33.1	33.1	4.7

[0050] So as to evaluate properties of the curable resin composition having thermal conductivity of the present invention, a (meth)acrylic resin type liquid A comprising as 100 parts by mass in total of (meth)acrylate monomers, composed of 58% (mass%, the same applies hereinafter) of 2-hydroxy-3-phenoxypropyl acrylate (ARONIX M-5700 manufactured by TOAGOSEI CO., LTD), 10% of p-cumylphenol ethylene oxide modified acrylate (ARONIX M-110 manufactured by TOAGOSEI CO., LTD), 30% of nonylphenol ethylene oxide 4 mol modified acrylate (ARONIX M-113 manufactured by TOAGOSEI CO., LTD) and 2% of liquid partially hydrated polybutadiene having both terminals methacryl-modified (TEAL-1000 manufactured by Nippon Soda Co., Ltd.), and 6 parts by mass of linseed oil as a drying oil, 1.25 parts by mass of cumene hydroperoxide (manufactured by NOF CORPORATION) as an organic peroxide, 0.2 part by mass of 2-methylene-bis(4-methyl-6-tertbutylphenol) as a polymerization inhibitor and 2.5 parts by mass of γ-methacryloxypropyltrimethoxysilane (A-174 manufactured by Nippon Unicar Company Limited) as a silane coupling agent, was obtained.

[0051] Then, spherical alumina in a desired amount as identified in Table 1 per 100 parts by mass of the (meth)acrylate monomers in the (meth)acrylic resin type liquid A was blended by using a planetary mixer/deaerator (MAZERUSTAR KK-100 manufactured by KURABO INDUSTRIES LTD.) to obtain a (meth)acrylic resin type liquid B containing spherical alumina. To the spherical alumina-containing (meth)acrylic resin type liquid B, as a decomposition accelerator for the organic peroxide, cobalt octanoate (manufactured by Kanto Fine K.K.) was added in an amount of 1.25 parts by mass per 100 parts by mass of the (meth)acrylate monomers to obtain a curable resin composition C. Properties of the obtained material were evaluated in accordance with the following methods. The results are shown in Table 2 (Example 1) and Table 3

(Comparative Example 1).

[0052]

TABLE 2

		Ex. 1					
Sample No.		1	2	3	4	5	6
Spherical alumina No.		I	I	I	II	III	IV
Amount of alumina (parts by mass)		400	280	600	400	400	400
Evaluation results	Viscosity (mPa·s)	8,000	3,500	13,000	9,200	6,800	9,100
	Curing time (min)	50	45	55	52	50	50
	Modulus in tension (MPa)	4.8	2.1	12	5.2	3.7	4.9
	Coefficient of thermal conductivity (W/m·K)	2.2	1.5	3.2	2.1	2.3	2.1
	Tensile lap-shear strength (MPa)	5.5	5.2	6.0	5.0	5.2	5.4

TABLE 3

		Comp. Ex. 1				
Sample No.		7	8	9	10	11
Spherical alumina No.		V	VI	VII	VIII	IX
Amount of alumina (parts by mass)		400	400	400	400	400
Evaluation results	Viscosity (mPa·s)	39,000	65,000	103,000	35,000	93,000
	Curing time (min)	50	53	52	46	45
	Modulus in tension (MPa)	4.5	4.8	5.5	4.7	4.6
	Coefficient of thermal conductivity (W/m·K)	2.1	2.0	2.3	1.9	1.9
	Tensile lap-shear strength (MPa)	4.2	3.8	0.9	4.0	1.2

(Evaluation methods)

[0053]

5 Viscosity: The viscosity of the curable resin composition C was measured by using a Brookfield viscometer at a temperature of 23°C.

Curing time: The time after the curable resin composition C was obtained until it lost fluidity and became a cured product at a temperature of 23°C was measured.

10 [0054] Modulus in tension: On a PET film, a frame punched out into a #1 dumbbell (JIS K7113) from a 2 mm thickness silicone rubber sheet was put, the curable resin composition C was cast, a PET film was placed thereon, followed by curing at a temperature of 23°C for 3 days, and the obtained cured product was removed from the frame to prepare a #1 dumbbell test specimen. The modulus in tension of the prepared test specimen was measured by using a universal testing machine at a rate of pulling of 5 mm/min.

15 [0055] Coefficient of thermal conductivity: The coefficient of thermal conductivity of a cured product of the curable resin composition C was measured by a laser flash measuring apparatus.

[0056] Tensile lap-shear strength: Measured in accordance with JIS K6580. Specifically, using as adherends aluminum test specimens (100 mm x 25 mm), two aluminum test specimens were bonded with an adhesion portion of 25 mm x 12.5 mm in width by means of the curable resin composition C, followed by curing at a temperature of 23°C for 24 hours to prepare a test specimen for evaluation of the tensile lap-shear strength. The tensile lap-shear strength of the prepared test specimen was measured by using a universal testing machine at a rate of pulling of 10 mm/min.

EXAMPLE 2

25 [0057] As an inorganic filler, four types of spherical silica having different particle size distributions were prepared. The peak diameters of each spherical silica in regions in the vicinity of from 0.2 to 1.5 μm , from 3 to 10 μm and from 30 to 70 μm are shown in Table 4.

TABLE 4

30	Spherical silica No.	Peak diameter (μm) in 0.2 to 1.5 μm	Peak diameter (μm) in 3 to 10 μm	Peak diameter (μm) in 30 to 70 μm	Mode diameter (μm)	Median diameter (μm)
	i	0.4	5.1	39.8	39.8	9.5
35	ii	0.7	7.5	55.1	55.1	12.0
	iii	0.3	15.5	38.8	38.8	17.6
	iv	0.1	Nil	38.8	38.8	35.3
40	v	0.7	3.2	33.1	33.1	4.7

[0058] In order to evaluate properties of a curable resin composition employing spherical silica as an inorganic filler, to 100 parts by mass of the (meth)acrylate monomers in the (meth)acrylic resin type liquid A used in Example 1, spherical silica in an amount as identified in Table 4 was blended in the same manner as in Example 1 to obtain a (meth)acrylic resin type liquid D containing spherical silica. To the (meth)acrylic resin type liquid D, as a decomposition accelerator for the organic peroxide, cobalt octanoate was added in an amount of 1.25 parts by mass per 100 parts by mass of the (meth)acrylate monomers to obtain a curable resin composition E. Properties of the obtained material were evaluated in the same evaluation methods as in Example 1. The results are shown in Table 5 (Example 2) and Table 6 (Comparative Example 2).

TABLE 5

		Ex. 2			
Sample No.		12	13	14	15
Spherical silica No.		i	i	ii	ii
Amount of silica (parts by mass)		220	300	220	300
Evaluation results	Viscosity (mPa·s)	6,700	9,700	5,000	8,900
	Curing time (min)	50	45	55	52
	Modulus in tension (MPa)	1.8	2.1	2.2	3.2
	Coefficient of thermal conductivity (W/m·K)	0.5	0.6	0.5	0.7
	Tensile lap-shear strength (MPa)	5.7	5.1	5.8	5.4

TABLE 6

		Comp. Ex. 2		
Sample No.		16	17	18
Spherical silica No.		iii	iv	v
Amount of silica (parts by mass)		220	220	220
Evaluation results	Viscosity (mPa·s)	36,000	53,000	48,000
	Curing time (min)	50	53	52
	Modulus in tension (MPa)	2.5	2.8	2.5
	Coefficient of thermal conductivity (W/m·K)	0.5	0.4	0.5
	Tensile lap-shear strength (MPa)	6.2	6.7	6.3

EXAMPLE 3

[0059] A spherical alumina-containing (meth)acrylic resin type liquid F was obtained, comprising 100 parts by mass in total of (meth)acrylate monomers, composed of 58% of 2-hydroxy-3-phenoxypropyl acrylate, 10% of p-cumylphenol ethylene oxide modified acrylate, 30% of nonylphenol ethylene oxide 4 mol modified acrylate and 2% of liquid partially hydrated polybutadiene having both terminals methacryl-modified, and 1.25 parts by mass of cumene hydroperoxide as an organic peroxide, 0.2 part by mass of 2-methylene-bis(4-methyl-6-tert-butylphenol) as a polymerization inhibitor, 2.5 parts by mass of γ -methacryloxypropyltrimethoxysilane as a silane coupling agent and 300 parts by mass of spherical alumina I as identified in Table 1. Then, linseed oil as a drying oil in an amount as identified in Table 7 was sprinkled per 100 parts by mass of the acrylate monomers in the spherical alumina-containing (meth)acrylic resin type liquid F to obtain an alumina-containing (meth)acrylic resin type liquid G. To the (meth)acrylic type liquid G, as a decomposition accelerator for the organic peroxide, cobalt octanoate was added in an amount of 1.25 parts by mass per 100 parts by mass of the (meth)acrylate monomers to obtain a curable resin composition H. The obtained material H was applied on a PET film in a thickness of about 1 mm, and the surface drying state after 12 hours was observed. The results are shown in Table 7.

TABLE 7

Sample No.	Ex. 3			
	19	20	21	22
Linseed oil (parts by mass)	0	7.5	15	35
Surface state	Filler Partially deposited	Favorable	Favorable	Partially uncured

EXAMPLE 4

[0060] To confirm heat cycle resistance of the curable resin composition of the present invention, a test specimen for evaluation of the tensile lap-shear strength was prepared by using the curable resin composition C sample No. 1 in the same manner as in Example 1, and the prepared test specimen was subject to a heat cycle test comprising repeatedly dipping the test specimen in liquid layers at -30°C and 150°C every 7 minutes by using a thermal shock tester (model: TSEL-2200-2, manufactured by ITEC Inc.). After 100, 500, 1,000, 2,000 and 3,000 cycles, the tensile lap-shear strength was measured in the same manner as in Example 1. The results are shown in Table 8.

COMPARATIVE EXAMPLE 4

[0061] A spherical alumina-containing (meth)acrylic resin type liquid I was obtained, comprising 100 parts by mass in total of (meth)acrylate monomers, composed of 30% of bisphenol A epoxyacrylate, 60% of dicyclopentenylxyethyl methacrylate and 10% of trimethylolpropane trimethacrylate, and 1.25 parts by mass of cumene hydroperoxide as an organic peroxide, 0.2 part by mass of 2-methylene-bis(4-methyl-6-tert-butylphenol) as a polymerization inhibitor, 2.5 parts by mass of γ -methacryloxypropyltrimethoxysilane as a silane coupling agent and 400 parts by mass of spherical alumina I as identified in Table 1. To the spherical alumina-containing acrylic resin type liquid J, as a decomposition accelerator for the organic peroxide, cobalt octanoate was added in an amount of 1.25 parts by mass per 100 parts by mass of the (meth)acrylate monomers to obtain a curable resin composition K (sample No. 23). The modulus in tension of the obtained curable resin composition K was 3,020 MPa. The curable resin composition K (sample No. 23) was subjected to a heat cycle test in the same manner as in Example 4. The results are shown in Table 8 together with the results in Example 4.

TABLE 8

Heat cycle test* Cycles		Tensile lap-shear strength (MPa)					
		0 cycle	100 cycles	500 cycles	1,000 cycles	2,000 cycles	3,000 cycles
Ex. 4	Sample No. 1	5.5	6.4	7.1	7.1	6.9	5.6
Comp. Ex. 4	Sample No. 23	12.3	1.2	Separated	-	-	-
*Heat cycle conditions: -40°C \leftrightarrow 150°C (7 min each)							

INDUSTRIAL APPLICABILITY

[0062] The curable resin composition of the present invention has fluidity and thereby is excellent in workability, and further, it provides a cured product which is flexible and has a low modulus, has high thermal conductivity to such an extent that heat generated from electronic components can be released, and has favorable heat cycle resistance. Accordingly, the curable resin composition can be applied to a potting material for sealing electronic components or an adhesive to be used for bonding heat spreaders or heatsinks in semiconductor packages. For such an application, it is advantageous in view of labor saving, energy saving and shortening of operation time and further, it is excellent in environmental resistance, and it is preferably applicable to this industrial field.

Claims

1. A curable resin composition comprising a (meth)acrylate monomer, an organic peroxide, a decomposition accelerator for the organic peroxide, and an inorganic filler, wherein the inorganic filler has a particle size distribution such that it has peak diameters at least in the respective regions of from 3 to 10 μm and from 30 to 70 μm , and the mode diameter is from 30 to 70 μm and the median diameter is from 5 to 40 μm .
2. A curable resin composition comprising a (meth)acrylate monomer, an organic peroxide, a decomposition accelerator for the organic peroxide and an inorganic filler, wherein the inorganic filler has a particle size distribution such that it has peak diameters at least in the respective regions of from 0.2 to 1.5 μm , from 3 to 10 μm and from 30 to 70 μm , and the mode diameter is from 30 to 70 μm and the median diameter is from 5 to 40 μm .
3. The curable resin composition according to Claim 1 or 2, which comprises from 0.5 to 10 parts by mass of the organic peroxide, from 0.1 to 10 parts by mass of the decomposition accelerator and from 100 to 1,500 parts by mass of the inorganic filler, respectively, per 100 parts by mass of the (meth)acrylate monomer.
4. The curable resin composition according to Claim 1, which further contains a drying oil.
5. The curable resin composition according to Claim 2, which further contains a drying oil.
6. The curable resin composition according to Claim 4 or 5, which comprises from 1 to 30 parts by mass of the drying oil, from 0.5 to 10 parts by mass of the organic peroxide, from 0.1 to 10 parts by mass of the decomposition accelerator and from 100 to 1,500 parts by mass of the inorganic filler, respectively, per 100 parts by mass of the (meth)acrylate monomer.
7. The curable resin composition according to any one of Claims 1 to 6, wherein the inorganic filler is spherical alumina.
8. A cured product made of the curable resin composition as defined in any one of Claims 1 to 7.
9. A potting material made of the curable resin composition as defined in any one of Claims 1 to 7.
10. An adhesive made of the curable resin composition as defined in any one of Claims 1 to 7.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2004/019118

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl.⁷ C08L33/06, C09J133/06, H01L23/29

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl.⁷ C08L1/00-101/14, C08F20/00-20/40

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI/L

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2002-309919 A (Denki Kagaku Kogyo Kabushiki Kaisha), 23 October, 2002 (23.10.02), Claims; Par. No. [0026] (Family: none)	1-10
Y	JP 2003-342021 A (Porima Tekku Kabushiki Kaisha), 03 December, 2003 (03.12.03), Claims; Par. No. [0003] (Family: none)	1-10
Y	JP 2001-139733 A (Kitakawa Kogyo Kabushiki Kaisha), 22 May, 2001 (22.05.01), Par. No. [0003] (Family: none)	1-10

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

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"&" document member of the same patent family

Date of the actual completion of the international search
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